



Electro-Deposition of Carbon Structures at Mid Voltage and Room Temperature Using Ethanol/Aqueous Solutions

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Direct syntheses of carbon structures including nanodiamond, microdiamond and diamond-like carbon (DLC) on silicon wafers by liquid phase electro-deposition are presented. The solution (ethanol/water) was employed as electrolyte at different concentration levels. Assays were carried out maintaining constant the electric potential between the silicon electrodes in the range of (80–300 V) at current density of approximately 2.0 mA/cm². Scanning electron microscopy showed that non-uniform, smooth and heterogeneous structures were produced. The structural composition was evaluated by micro-Raman spectroscopy. A mechanism for the formation of sp³ and sp² hybridizations is proposed.

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Diamond and carbon related materials have been considered promising materials for many industrial applications due to their superb physicochemical properties such as high hardness, low friction coefficient, wear resistance, high thermal conductivity, chemical inertness, and good biocompatibility, among others.^{1–4} Diamond and carbon related materials have been produced by a variety of chemical vapor deposition techniques (CVD),^{1,2} as well as the low temperature deposition process, such as the electro-deposition.^{3,4}

The first attempt to grow carbon films by electro-deposition technique was reported by Namba⁵ and ever since that, others groups have used such technique for carbon films preparation.^{3–14} Sreejith et al. obtained diamond-like carbon (DLC) at low voltages (80–300 V) and 1 mm interelectrode separation, which gives electric fields of 0.08–0.3 Vm⁻¹.¹¹ Graphite and silicon were employed as electrodes (anode/cathode) and ethanol as electrolyte. It is still not clear whether the carbon film deposited had as its source the electrolyte, or the graphite electrode itself or both.

In this work we report the results of our investigation on electro-deposition of carbon films containing nanodiamond and diamond inclusions, diamond-like carbon (DLC) and graphitic phases on silicon wafers, which were submerged in an aqueous ethanol solution. All assays were run at room temperature, without heating or cooling and with a low energy consumption. Raman spectra and scanning electron microscopy images are presented and discussed, and a mechanism for the formation of the sp³ and sp² hybridization/bonding is proposed.

Experimental

Mirror polished pieces of *n*-type silicon (100) with resistivity of about 1 Ω.cm and dimensions of 30 × 10 × 0.3 mm³ were used as electrodes (anode and cathode). Prior to deposition process, the silicon substrates were cleaned by ultrasonic treatment in acetone for 30 min. The electrolyte was a solution constituted of analytical grade Merck[®] ethanol and deionized water. The solution was not agitated during the deposition process. The distance between the electrodes was fixed at 25 mm, the same value for all experiments. The voltage applied between the electrodes was maintained constant during each experiment and ranged from 80 V to 300 V. Heating or cooling was never applied, so the temperature of the system had a slight increase during the first fifteen minutes, remaining constant until the end of the experiment. In all cases the duration of the experiment was 5 h and 30 min. and the measured current density was about 2.0 mA/cm². Only on the negative electrode was observed the formation of

dispersed structures. Morphological images were taken using a JSM 5900 LV scanning electron microscope. For chemical analysis a Renishaw[®] InVia Raman microscope system was used. The micro-Raman measurements were carried out at room temperature employing 785 nm and 514.5 nm laser wavelengths. All samples were characterised by mapping point-by-point micro-Raman scattering.

Results and Discussion

The electro-deposition cell used an aqueous solution of ethanol as the electrolyte. Table I presents parameters of these depositions. Nanodiamonds, diamonds, DLC and amorphous carbon were directly deposited on silicon wafers without any pre-treatment, except an acetone cleaning process.

Typical scanning electron microscopy images at different magnifications of these as-deposited samples are shown in Figure 1. Images (A) and (B) correspond to sample type (d); images (C) and (D) correspond to sample type (a); image (E) correspond to sample type (c) and image (F) correspond to sample type (b). The deposited structures have no coalescence or uniformity. Some features appears nanocrystalline with cubic grains. Apparently there is no morphological differences between the samples, when they are compared with the same magnifications. To better investigation of these structures, micro-Raman spectroscopy was employed.

Typical Raman spectra of samples, obtained from mapping, with short intervals of point-by-point analysis are depicted in Figure 2. Usually a laser of 514.5 nm was employed, except for type (a) sample. An intense peak around 1332 cm⁻¹, which corresponds to sp³ carbon hybridization of natural diamond, is present in almost all spectra of Figure 2. The frequency shift ranges from 1325 cm⁻¹ to 1340 cm⁻¹ indicating the presence of some kind of intrinsic or extrinsic stress.¹⁵ In Figure 2e a peak at 1325 cm⁻¹ is observed and this may be also assigned to a diamond (hexagonal) like structures.^{16,17} Broad bands centered around 1350 cm⁻¹ and 1600 cm⁻¹ correspond to D-band and G-band, respectively. The D-band appears in the range

Table I. Selected parameters of electro-deposited carbon.

Sample Description	Applied Potential (V)	Ethanol: Water (% v/v)
Type (a) (DLC and Nanodiamond)	80	98/2
Type (b) (DLC and Diamond)	200	98/2
Type (c) (DLC)	300	70/30
Type (d) (Diamond and Graphite)	300	30/70

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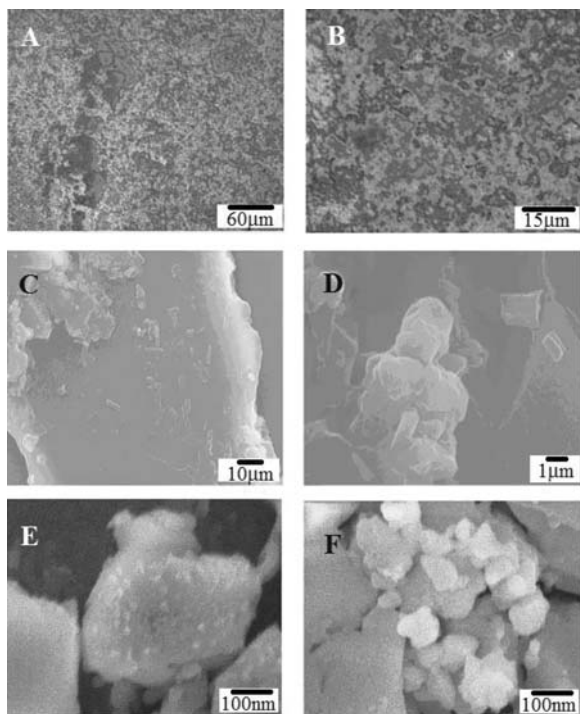


Figure 1. Typical scanning electron microscopy images of as-deposited carbon structures: (A) and (B) correspond to sample type (d), (C) and (D) correspond to sample type (a), and (E) and (F) correspond to type (c) and type (b), respectively.

of 1347 cm^{-1} to 1352 cm^{-1} , is attributed to a disorder-induced mode arising due to zone boundary phonon of A_{1g} symmetry (disordered graphite).¹² The G-band appears around $1531\text{--}1655\text{ cm}^{-1}$ and is associated with the bond stretching of all pairs of sp^2 bonds in both rings and chains, corresponding to the optical zone center phonon of E_{2g} symmetry, characteristic of graphite type materials.^{13,14} These bands reveal the presence of graphite and amorphous carbon. In Figure 2c and 2d the spectra were obtained using 785 nm laser excitation which is more sensitive for sp^2 carbon hybridization. The Raman shift in these spectra show peaks and broad bands centered at $1128\text{--}1140$, 1209 , $1317\text{--}1340$, $1347\text{--}1352$, 1424 , 1450 , 1531 , 1550 , $1589\text{--}1596$, 1609 and 1655 cm^{-1} . The nature of the peak at 1140 cm^{-1} has been of some controversy since some authors believe that it is associated to nanocrystalline diamond^{1,18} and others attribute this peak to *trans*-polyacetylene (sp^2 carbon) located at grain boundaries, where the polyacetylene would be present^{18,19} Pfeiffer et al. heated at temperatures of 500°C and 1200°C and concluded that the modes 1150 cm^{-1} and 1480 cm^{-1} disappeared.¹⁹ They assume that these modes originate from short *trans*-polyacetylene segments since *trans*-polyacetylene is known to be unstable at high temperatures. Unspecified observed peaks at 1317 cm^{-1} and 1531 cm^{-1} would be related to amorphous carbon. P. W. May et al. related peaks in the range of 1459 cm^{-1} to 1465 cm^{-1} to *trans*-polyacetylene.²⁰

The results presented in this work have demonstrated that it is possible to deposit a mixture of amorphous carbon, graphite, DLC, microdiamond and nanodiamond on silicon substrates with low voltage and close to room temperature. The structures deposited have been of non-homogeneous films and with low deposition rates, of around $0.1\text{ }\mu\text{m}\cdot\text{h}^{-1}$. We believe that the existence of non-uniformity may be related to the growth conditions adopted that still need to be optimized. With better understanding of the deposition mechanism of these materials, it will be find a way to grow homogeneous films

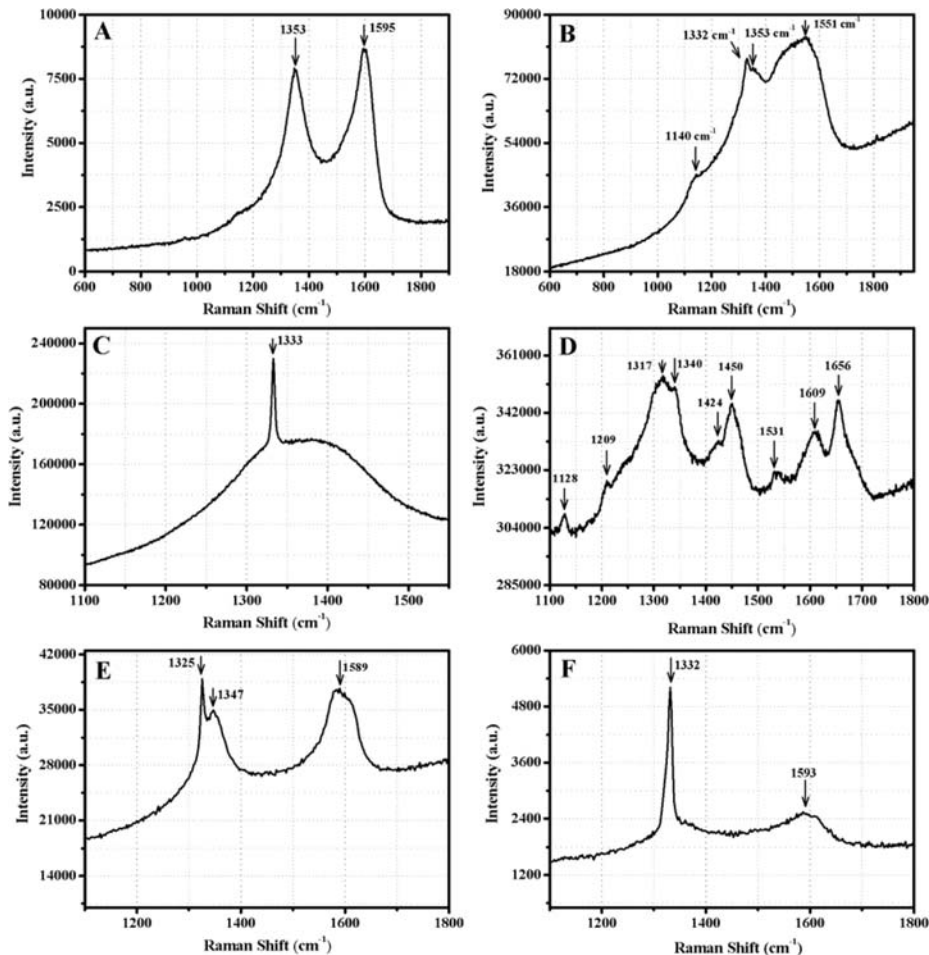
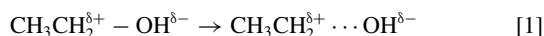


Figure 2. Typical Raman spectra of as-deposited samples: (A) and (B) correspond to the same sample type (a). (C) and (D) correspond to same sample type (b). (E) corresponds to sample type (c). (F) corresponds to sample type (d). For sample type (b) (C and D) a 785 nm wavelength laser was applied point by point. For images A, B, E and F a 514.5 nm laser wavelength was employed.

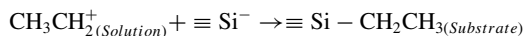
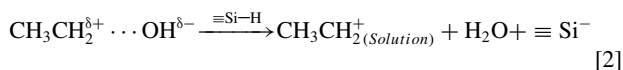
with uniform composition at temperatures close to the room temperature. The electrolyte plays a very important role in the film growth process. When it consists of deionized water with alcohol, the water interacts in two ways: (i) it can participate in the formation of dynamic hydrogen-bonded chains, thereby raising the polarizability, and; (ii) it can form relatively stable structures such as $\text{H}_2\text{O}(\text{ROH})_4$ which have zero net dipole moment and consequently diminish volume polarizability, can perhaps help sp^3 carbon hybridization in liquid phase electro-deposition technique.²¹

The electro-deposition chemical mechanism of carbon materials is not known, however some mechanisms have been proposed to describe diamond growth.^{11,14,22-24} A mechanism for this process using methanol as organic electrolyte was proposed by He et al. and Zhu et al.^{22,24} Sreejith et al. showed a mechanism based in ethanol as organic electrolyte.¹¹ The mechanism presented in this work is based on empirical observations (presence of *trans*-polyacetylene), and on the formation of precursor ions and gas products in the solution, as reported by some authors.^{11,14,22,24}

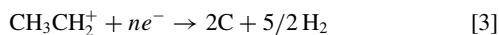
Using ethanol as the electrolyte there is a strong possibility that ethanol molecules are polarized under an applied potential, as can be demonstrated by Equation 1:



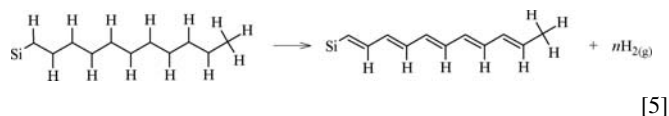
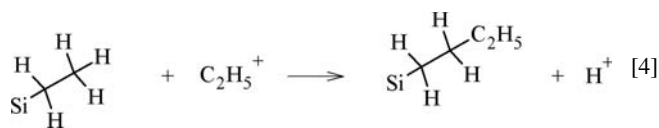
In the cathode (hydrogen-terminated silicon surface), the molecule positive pole is bonded to the Si surface by replacement of the hydrogen linked to the Si. Further, the ionization of ethanol (loss of OH) occurs by the attacking of hydrogen ion removed over the oxygen bonded to carbon. In the present case, the reaction is given in Equation 2:



In the cathode (substrate) the major step is the dehydrogenation of ethyl that occurs via electrooxidation reaction (Equation 3):



A mechanism that can occur is the coupling of ethyl groups over the substrate. In this case, ethyl ions are inserted into the C-H bond elongating the carbon chain (Equation 4). The subsequent dehydrogenation leads to the formation of DLC, diamond or, as presented in the Equation 5, *trans*-polyacetylene.



Sreejith et al. propose that bond could also be formed between a carbon and other adjacent carbon on the substrate surface, thus propagating the chain both along the substrate and away from the substrate.¹¹

Although the reasonability of this modeling, it should only be regarded as a simplified approximation to the real reaction. A significant observation in the present study is the formation of diamond and diamond-like phases at lower voltages and temperatures compared to the literature values.

Conclusions

Carbon structures such as nanodiamonds, DLC and amorphous carbon were directly deposited on silicon substrates without any pre-treatment. Micro-Raman spectra and scanning electron microscopy showed characteristics of non-uniform materials, besides a small and dense deposited area. This phenomena may be related to the growth conditions and could be optimized in future works. Low temperature electro-depositions are still not consolidated, because the low growth rate and non-uniform formation. Further investigation is required in order to develop an efficient method to deposit more homogeneous films.

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